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OF CARBON BLACKS GRAPHITIZED AT
SUCCESSIVELY HIGHER TEMPERATURES**

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OFFICE OF NAVAL RESEARCH

Technical Report

Number 3

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R. A. Beebe,² D. M. Young³ and H. Bienes

SUMMARY

The calorimetric heats of adsorption have been measured for argon at -195°C on a series of carbon blacks graphitized at the successively higher temperatures, 1000° , 1500° , 2000° and 2700°C . X-ray and electron microscope studies reported by Schaeffer et al, indicate increasing degree of graphitisation with increasing temperature of heat treatment; this would result in increasingly homogeneous surfaces within the series. Our experimental results provide an interesting exhibit of the mode of change in the differential heats of adsorption curves as we go from the heterogeneous surface of the parent Spheron black through successive stages to the most homogeneous surface of the sample treated at 2700°C . These results may be correlated with the stepwise isotherms found by Polley et al on the same series of blacks.

There is an increasing body of experimental data which shows rather sharp differences in the characteristics of physically adsorbed films on heterogeneous and on more homogeneous surfaces. Differences of this sort are especially apparent in the heat-coverage curves for the adsorption of gases on such surfaces. These differences may be illustrated by the work on carbon blacks previously reported from this laboratory. In particular two nonporous blacks⁴ have been extensively studied.⁵ One of these, known commercially as Spheron 6, is a rubber reinforcing channel black; the other, designated as Graphon, is produced by heat treatment of the Spheron 6 at electric furnace temperatures, approximately 3000°C .

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- (1) Presented before the Division of Physical and Inorganic Chemistry at the 122nd National Meeting of the American Chemical Society in Atlantic City, N. J., September 1952.
 - (2) Professor of Chemistry, Amherst College, Amherst, Mass.
 - (3) Present address, National Research Council, Ottawa, Canada.
 - (4) The conclusion that these pigments are essentially nonporous is based on a comparison of the surface areas determined by the B.E.T. nitrogen adsorption method and computed from the particle diameters as estimated by means of the electron microscope.
 - (5) a) Beebe, Millard and Cynarski, J. Am. Chem. Soc., **75**, 839 (1953).
b) See also Technical Report Number 1 by these authors.

The X-ray studies of Biscoe and Warren⁶ have shown that, in contrast to the parent material Spheron, the Graphon possesses a much higher degree of order in its three dimensional structure with indication of a partial graphitization during the above heating process. From the adsorption studies it is apparent that, in comparison with Spheron 6, the Graphon has a relatively homogeneous surface.⁵ Probably as a result of this homogeneity and the consequent opportunity for easily observing the effects of lateral interaction between adsorbed molecules, there are characteristic humps in the isotherms and maxima in the heats of adsorption vs. coverage curves for both nitrogen and argon.⁵

Schaeffer, Smith and Polley⁷ have reported the preparation of a series of carbon blacks starting with Spheron 6 by graphitizing at successively higher temperatures up to 2700°C. This provides an interesting series in which there is a gradual change from a heterogeneous surface to successively more homogeneous surfaces.

Polley, Schaeffer and Smith⁸ have measured the isotherms for argon on several series of these heat treated blacks. Their data show a progressive change, with increasing graphitization temperature, from a normal Type II isotherm to isotherms of stepwise character. These authors point out that the stepwise isotherms are precisely the type which would be expected for adsorption on homogeneous surfaces, and cite the predictions of Fowler and Guggenheim,⁹ of Halsey¹⁰ and of Hill.¹¹ The humps in the isotherms are attributed to interaction between adsorbed molecules.

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- (6) Biscoe and Warren, J. Applied Phys., 13, 364 (1942).
 - (7) W. D. Schaeffer, W. R. Smith and M. H. Polley, Ind. Eng. Chem., forthcoming publication.
 - (8) M. H. Polley, W. D. Schaeffer and W. R. Smith, J. Phys. Chem., 57, 469 (1953).
 - (9) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics." Cambridge University Press, England, 1939, pp. 426-444.
 - (10) a) G. D. Halsey, Jr., J. Am. Chem. Soc., 73, 2693 (1951); *ibid.* 74, 1082 (1952).
 - (11) T. L. Hill, J. Chem. Phys., 15, 767 (1947).

Because heat data are more susceptible to theoretical interpretation than are the isotherms alone, we have undertaken a calorimetric study of the series of graphitized Spheron carbon adsorbents.¹² Moreover the heats of adsorption studies bring out differences in the monolayer, below $V/V_m = 1$, which are not apparent from the work of Polley et al.

Experimental

Materials.— The parent material, Spheron 6, is an essentially nonporous commercial channel black with specific surface area 114 sq. m. per g. as determined by nitrogen adsorption. The other four samples which shall be designated as Spheron (1000°), Spheron (1500°), Spheron (2000°) and Spheron (2700°) were prepared by heat treatment of the Spheron 6, at the temperatures indicated, for a period of two hours.¹³ The details of preparation and the results of X-ray and electron microscope studies of the structure of the heat-treated carbon blacks have been reported elsewhere.⁷ The surface areas of the heat-treated series are given in Table I of the paper by Polley, Schaeffer and Smith;⁸ our blacks were identical with the Spheron samples used by these investigators.

The argon used in the adsorption measurements and the helium used in estimating the dead space in the adsorption system were obtained from the Air Reduction Sales Company in the highest degree of purity available. No further purification of these gases was attempted. All the adsorption measurements were made at liquid nitrogen temperature.

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- (12) Polley, Schaeffer and Smith have prepared three series of graphitized blacks in addition to the Spheron series which we have studied. In one of these series in particular, which was derived from a furnace black (P-33) the sample graphitized at 2700°C appeared to have a considerably more homogeneous surface than that of the Spheron (2700°). Unfortunately the specific surface areas of the P-33 series were too small to give us sufficient definition in the calorimetric values. For that reason we were forced to be content with studying the Spheron series.
- (13) The graphitized blacks were of necessity exposed to air during storage and during transfer to the calorimeter. Experiments now in progress in this laboratory indicate that any oxygen which might have been chemisorbed during such exposure, would have been removed by our procedure of outgassing at 200°C.

Apparatus and Procedure.-- The calorimeter and system of gas buret and manometer were identical with those previously used.⁵ The calorimeter design was particularly well adapted to the present problem because the inner platinum bucket of the calorimeter could be removed for changing samples of adsorbent. Each adsorbent sample was outgassed in the calorimeter at 200°C for at least 24 hours prior to the adsorption measurements.¹⁴ With the exception of Spheron (2000°) one complete heat run consisting of from 12 to 15 increments was made for each adsorbent. With the Spheron (2000°) black, one complete run and parts of two other runs were carried out.

As explained in a previous publication,⁵ the heats as measured are isothermal heats as defined by Hill¹⁵ and Kington and Aston.¹⁶ Our measured heats would differ from the isosteric heats by a factor $V_G(\partial p/\partial N_g)_T$ where V_G is the volume of the dead space in the calorimeter and $(\partial p/\partial N_g)_T$ is the slope of the isotherm. This term never exceeded 10 cal./mole in any increment of any heat run of the present investigation. Since the quantity $V_G(\partial p/\partial N_g)_T$ is in all cases less than the estimated experimental error ($\pm 3\%$), this quantity has not been subtracted from the calorimetrically measured heats in obtaining the q_{st} values for the isosteric heats shown in Fig. 2.

Results

The results of the experimental work with argon on the four heat-treated carbon blacks are given graphically in Figs. 1 and 2. In Fig. 1, are shown the isotherms for the original Spheron and for the samples treated at 1000° and 2700°C. To avoid complication, the isotherms for argon-Spheron (1500°) and argon-Spheron (2000°) have been omitted from

(14) Polley, Schaeffer and Smith⁸ have shown that the use of outgassing temperatures of 200°C and of 1000°C resulted in identical isotherms in the case of the heat-treated carbon blacks. They point out that this observation is at variance with that of Gulbransen and Andrew [Ind. Eng. Chem., 44, 1039 (1952)], in the experiments of the latter investigators with graphite.

(15) T. L. Hill, J. Chem. Phys., 17, 520 (1949).

(16) Kington and Aston, J. Am. Chem. Soc., 73, 1929 (1951).

Fig. 1. Actually these isotherms fit nicely into the general picture, as the volumes adsorbed at a given pressure up to $p/p_0 = 0.4$ decrease for the different samples in the order Spheron (1000°), Spheron (1500°), Spheron (2000°) and Spheron (2700°). Above $p/p_0 = 0.4$, the volumes adsorbed at a given pressure show an increase in going from Spheron (1000°) through Spheron (1500°) to Spheron (2000°) and finally to Spheron (2700°). These isotherms check with those of Polley, Schaeffer and Smith⁶ for the same adsorption system. The heat-coverage curves are shown in Fig. 2. The data on Spheron (untreated material) shown in Figs. 1 and 2 for comparison are taken from previous work in this laboratory.⁵ The heat curve for argon on Spheron 6 is represented by the dotted line in Fig. 2.

Discussion

For the sake of clarity in interpreting the experimental results represented in Fig. 2, the discussion will be divided into a consideration of the various regions of coverage as given below.

1. Beginning of the first layer ($V/V_m = 0$ to 0.4).— In this region the differential heats undergo a regular decrease with temperature of graphitization up to 2000°C, but no further change in the region between 2000° and 2700°C. It has been suggested in a previous publication⁵ that the initial high heats found for nitrogen or argon adsorption on Spheron may be due to adsorption in narrow, shallow depressions at the grain boundaries between parallel layer groups in the surface. With graphitization, the growth of the parallel layer groups and the increasing degree of order within these groups would tend to reduce the total length of the above depressions as well as their depth. It is reasonable to believe that such a change would result in increasingly lower initial heats of adsorption with increased graphitization.

Because there is definite evidence of lateral interaction in the second half of the monolayer (see below), it seems probable that this interaction may to some degree be in effect on a relatively bare surface. It may be that without any lateral interaction the heats in the region $V/V_m = 0$ to 0.4 would fall lower than they do experimentally.

2. Second part of the first layer ($V/V_m = 0.4$ to 1.0).-- In this region, the arrest in the heat-coverage curves, only slightly apparent for Spheron 6 of Fig. 2, changes into a maximum for the Spheron (1000°) sample and this maximum becomes progressively higher in passing from Spheron (1000°) on up to Spheron (2700°).

In earlier work⁵ an attempt has been made to explain the relative behavior of Spheron and Graphon on the assumption that the surface of the former is energetically heterogeneous and that of the latter more homogeneous. On Spheron, the decrease in the heats with increasing coverage would then be attributed to the predominating effect of surface heterogeneity, while on the more homogeneous graphon, lateral interaction, the effect of which is no longer obscured by that of heterogeneity, is evidenced by the resultant increase in differential heat with coverage, especially at $V/V_m = 0.5$ to 1.0 . It is quite reasonable then that the maximum due to this lateral interaction should become increasingly prominent as the carbon black becomes more graphite-like with heat treatment.

Young and Crowell¹⁷ have shown that the energy of binding for argon on the basal planes of graphite is virtually the same for all probable positions of the argon atom relative to the surface carbon atoms of the graphite lattice. This means that such a graphite surface would represent a system of non-localized sites for argon adsorption and would tend to permit the formation of a hexagonally close-packed monolayer of argon. It is probable that the Spheron (2700°) surface would approach but would not become identical with such a system of non-localized sites on basal planes of graphite.¹⁸

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- (17) A. D. Crowell and D. M. Young, Trans. Faraday Soc., forthcoming publication.
 - (18) The X-ray studies of the series of carbons used in the present investigation show that the samples which were graphitized at the higher temperatures approach graphite in their crystallite structure. With increasing temperature of graphitization the crystallites within the carbon black particles increase in size as well as achieving more nearly perfect ordering of the three dimensional array of carbon atoms.⁷ Furthermore, the electron microscope reveals that while the parent Spheron particles are roughly spherical in shape, the graphitized samples such as Spheron (2700°) have developed flat sides due to the growth of the crystallites or parallel layer groups.⁷ It seems possible that these flat sides are basal graphite planes, although we have no conclusive evidence that this is true.

Orr¹⁹ has calculated the maximum energy of interaction between an argon atom and its six nearest neighbors in a hexagonally close-packed monolayer adsorbed on a surface of non-localized sites. Using Orr's method as corrected by Young,²⁰ we obtain 1580 cal./mole for the interaction energy. This is more than twice the increase in the experimentally observed heats in the second half of the monolayer for Spheron (2700°), the most homogeneous member of the series of carbon adsorbents under investigation.

This discrepancy between the theoretical value for interaction and the experimentally observed height of the maximum in the first layer, is probably due to some residual heterogeneity in the graphitized carbon surface. For a valid comparison with the theoretical value we should consider the rise in heats on a homogeneous carbon surface all the way from $V/V_m = 0$ to $V/V_m = 1.0$. High initial heats due to heterogeneity at low coverage would tend to offset the absence of lateral interaction with the result that the observed rise in heats in the region from $V/V_m = 0.4$ to $V/V_m = 1.0$ would not represent the whole of the interaction energy. Moreover any lack of homogeneity in the surface would tend to lower the absolute value of the heats near $V/V_m = 1$ because there would be no sharp separation between the first and second layers.²⁰

Mooi, Pierce and Smith²¹ have determined the isosteric heats for ethyl chloride on Graphon in the temperature region of -78 to 75°C. They comment that in general shape their curve for heats vs. volume adsorbed resembles those previously reported for nitrogen on Graphon at -195°, ^{22,23,24} but that the maximum in the region of V_m is higher and sharper for ethyl chloride than for nitrogen. It is true that the absolute height of the maximum for ethyl chloride is over twice the height of the maximum in the nitrogen heat

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- (19) W. J. C. Orr, Proc. Roy. Soc. A. 173, 349 (1939).
 - (20) D. M. Young, Trans. Faraday Soc., 48, 560 (1952).
 - (21) J. Mooi, G. Pierce, and R. N. Smith, J. Phys. Chem., 57, 52 (1953).
 - (22) R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, J. Am. Chem. Soc., 69, 95 (1947).
 - (23) L. G. Joyner, and P. H. Emmett, J. Am. Chem. Soc., 70, 2353 (1948).
 - (24) T. L. Hill, P. H. Emmett and L. G. Joyner, J. Am. Chem. Soc., 73, 5102 (1951).

curve. However, if we consider the above maxima on a basis relative to the total heats of adsorption, we see that the height of the maximum represents a smaller fraction of the total heat for ethyl chloride than for nitrogen. Such an effect may be due to the higher temperature of the ethyl chloride adsorption or to a less favorable packing of the larger molecules of this adsorbate as suggested by Mooi et al in their discussion of the absence of a hump at $2 V_m$ in the ethyl chloride isotherm. It would appear that the conditions for observing the effect of lateral interaction on Graphon are less favorable for both ethyl chloride and for nitrogen than they are for argon since the maximum in the heat curve on the relative basis discussed above is highest in the case of argon.

3. The transition from the first to the second layer ($V/V_m = 1$).-- Not only is there an increase, with temperature of graphitization, in the heights of the maxima of Fig. 2 at the end of the first layer, but also the slope of the curves near V_m increases with increased graphitization. This evidence points to an increasingly sharp separation between the first and second layers on the increasingly homogeneous samples of graphitized carbon black.

4. The region above V_m .-- A second maximum which becomes more pronounced with degree of graphitization is revealed in Fig. 2, corroborating the results previously obtained in this laboratory.⁵ It is of interest that Mooi, Pierce and Smith¹⁷ have recently reported a low second maximum for ethyl chloride on Graphon.

It is seen from Figs. 1 and 2 that the characteristics of the isotherms and heat-coverage curves have been considerably altered by heat treatment at 1000° . In a previous investigation²² it was found that the heat treatment at 927°C had little effect on either the isotherm or the heat-coverage curve as was attested by the similarity in adsorption characteristics of the Spheron 6 and the "devolatilized" Spheron (927° treated). It was pointed out in the earlier work^{22,25} that most of the chemisorbed oxygen on the Spheron 6 had

(25) R. B. Anderson and P. H. Emmett, J. Am. Chem. Soc., 56, 753 (1952).

been removed even by heating to 927°C and it was inferred that the underlying structure of the black had been little altered by the heat treatment. On the basis of the above observations we may conclude that a considerable change in the physical state of the surface has occurred during heat treatment in the range between 927°C and 1000°C. Structural changes in the carbon blacks in this temperature range have been discussed by Polley et al.⁶ From the work reported by Schaeffer and his co-workers⁷ it appears that the major graphitization changes occur between 1000°C and 2000°C. This temperature range of heat treatment also produces a large change in the adsorption characteristics as is seen from Fig. 2.

Acknowledgement

Our thanks are due to Mr. W. D. Schaeffer who prepared the new series of blacks and to Dr. W. R. Smith who called them to our attention. We are also indebted to Dr. A. D. Crowell for helpful discussions in the interpretation of our results.

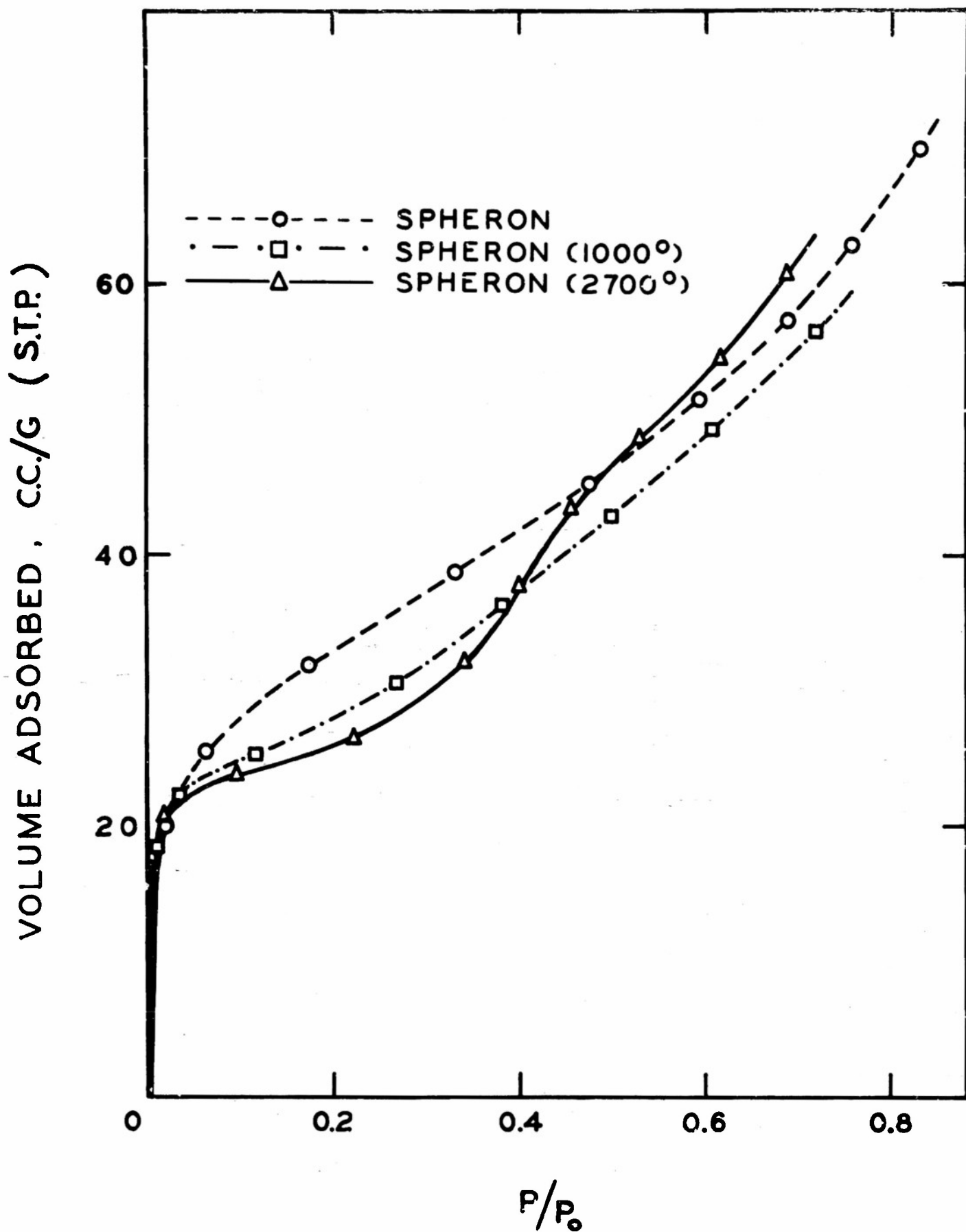


FIG. 1. ISOTHERMS, ARGON ON CARBON BLACKS AT -195°C .

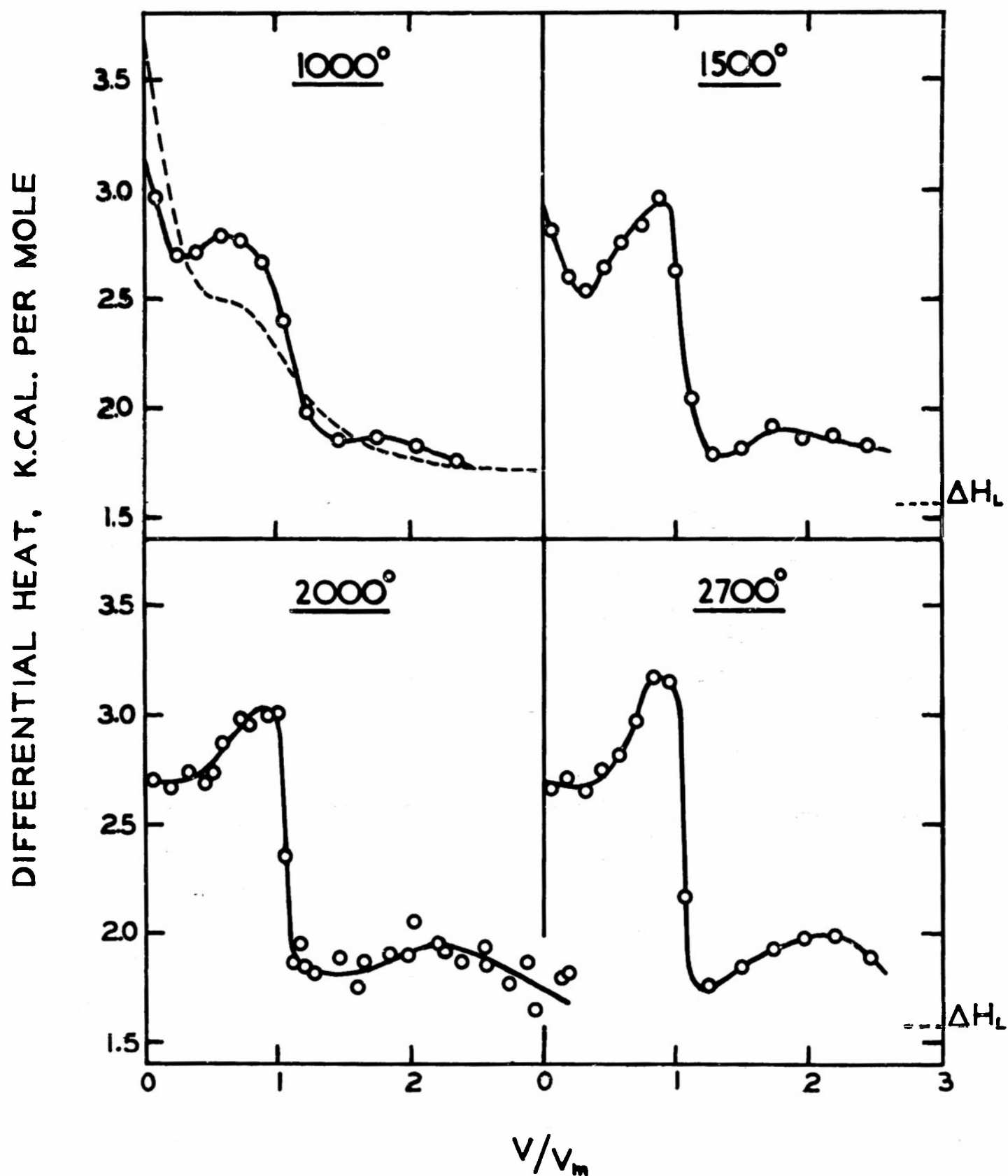


FIG. 2. HEATS OF ADSORPTION OF ARGON ON CARBON BLACKS AT -195°C . DOTTED LINE REPRESENTS UNTREATED BLACK. TEMPERATURES OF GRAPHITIZATION ARE INDICATED.